## An Iron(II) Spin-Transition Compound with Thiol Anchoring Groups

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The synthesis and characterisation of the complex  $[Fe^{II}(L)_2]$ -(ClO<sub>4</sub>)<sub>2</sub> [L = S-(4-{[2,6-(Dipyrazol-1-yl)pyrid-4-yl]ethynyl}phenyl) ethanethioate] carrying both a spin-transition core and acetyl-protected terminal thiol groups is described. The compound exhibits a reversible, thermally driven solid-state spin transition at 277 K with a hysteresis loop of ca. 8 K. The

## Introduction

Molecular spin-transition (ST) units made of iron(II) metal ions in an octahedral coordination environment may be considered as potential electronic components<sup>[1]</sup> in the construction of switching molecular devices in different dimensional scales (thin films, SAMs, nanoparticles, -wires, etc.) since their physical properties change strongly in dependence on their intrinsic spin states. The electronic ground state of an ST unit is represented by the low-spin (LS) state, while excitation leads to the metastable high-spin (HS) state. The spin switching is basically a result of the intraorbital electron-density reorganisation within the iron(II) metal ion. The observed molecular mechanical movement (elongation  $\leftrightarrow$  contraction) during spin transition is caused by the population of antibonding e<sub>g</sub>\* orbitals in the HS case, which leads to Fe-N bond length variations of approximately 0.2 Å. The spin-state switching is entropydriven and can be reversibly triggered by external parameters like temperature, pressure and electromagnetic radiation (visible light, X-ray, etc.).

The shaping of ST units for possible use in molecular electronic nanodevices (e.g. switching arrays, wires, etc.) is receiving growing interest. This rising interest is strongly driven by the spin-state-dependent electronic, magnetic, photophysical, and mechanical properties of ST compounds. The vast majority of the studies dealing with iron(II) spin-transition compounds has been carried out under solid-state bulk conditions.<sup>[1–5]</sup> Only a small number of

unique combination of the bistable spin-transition property with thiol anchoring groups sets the basis for the investigation of the spin-transition switching phenomenon at a singlemolecule level.

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publications demonstrate the principle of the spin-state transition process in different environments or dimensions. For example, (i) in polymeric matrices,<sup>[1a]</sup> (ii) in surface-grown iron(II) coordination polymer-based multilayer thin films,<sup>[6]</sup> (iii) in Langmuir–Blodgett (LB) multilayers of monomeric and metallo-supramolecular polymeric complexes<sup>[7]</sup> and (iv) in nanoparticles of Fe<sup>II</sup> complexes.<sup>[8]</sup>

Furthermore, an important ingredient of the nanodevice "tool box" is the molecular wire concept, where the current/voltage (I/U) characteristics of single molecules are investigated between Au electrodes.<sup>[9]</sup> Such molecular wires are designed, synthesized and studied at a single-molecule level to scrutinize the effect of external stimuli such as electric field, laser light, molecular conformational changes, molecular symmetry and temperature on the single-molecule electric transport.<sup>[10]</sup>

In this vein, ST centres are of interest because they are some of the best-known forms of inorganic electronic switches. However, exploitation of the real potential of the ST complexes to construct a switching magnetic nanocomponent is still in its infancy due to the design and more notably to synthetic challenges. To the best of our knowledge no report is available on the synthesis of an ST complex bearing thiol anchoring groups based on a molecular wire concept.

In order to manipulate iron(II) ST units under surface conditions, we have rationally designed and synthesized the complex [Fe<sup>II</sup>(L)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (1) [L = *S*-(4-{[2,6-(dipyrazol-1yl)pyrid-4-yl]ethynyl}phenyl ethanethioate]. Compound 1 consists of three main components: (i) an octahedral iron(II) ST unit,<sup>[5]</sup> (ii) two highly  $\pi$ -conjugated phenylethynyl linker moieties and (iii) two acetyl-protected thiol anchoring groups to facilitate contact with noble and coinage metal (gold, silver, mercury, copper, palladium and platinum) electrodes or surfaces upon deprotection of the acetyl groups (Scheme 1).



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Scheme 1. Schematic cartoon representation of the spin transition molecule  $[Fe^{II}(L)_2](ClO_4)_2$  (1) with thiol anchoring groups.

#### **Results and Discussion**

We have achieved the synthesis of our target ligand L in eight steps starting from citrazinic acid. The synthesis of the 4-iodo-2,6-di(pyrazol-1-yl)pyridine precursor 2 (Scheme 2) was recently reported by us.<sup>[2]</sup>

Starting from this iodo precursor, two subsequent Sonogashira coupling reactions were employed to introduce the conjugated phenylethynyl linkers: First, the connection of a  $\pi$ -conjugated ethynyl moiety at the 4'-position of the 2,6di(pyrazol-1-yl)pyridine backbone was established, followed by the coupling of a (thioacetyl)benzene group to the deprotected ethynyl linker. The precursor of the anchoring group 4-iodo-1-(thioacetyl)benzene was prepared as reported in the literature.<sup>[11]</sup> Due to deprotection of the acetyl group leading to the formation of dimeric dithiol coupling side products, the final yield of L was only 20%. The purification of ligand L was carried out on a silica gel column. The metal coordination reaction was achieved in a mixture of dichloromethane and methanol at room temperature from 1 equiv. of Fe<sup>II</sup>(ClO<sub>4</sub>)<sub>2</sub> hydrate and 2 equiv. of ligand



Scheme 2. Synthesis of ligand L and its iron(II) molecular complex 1. Reagents and conditions: (a)  $Pd(PPh_3)_4/CuI/Et_3N/thf/N_2$ , (b)  $K_2CO_3/MeOH/CH_2Cl_2$ , (c)  $Pd(PPh_3)_2Cl_2/CuI/iPr_2NEt/thf/N_2$ , (d) FeClO<sub>4</sub> hydrate.

L yielding a dark-red single-crystalline material in 58% yield (Scheme 2).<sup>[5]</sup> Recrystallization was carried out in methanol, and the obtained red crystals were used for X-ray diffraction and magnetic studies.

Single-crystal X-ray diffraction analysis revealed the triclinic space group  $P\overline{1}$  of 1 (Figure 1). In the crystal lattice, each molecular complex 1 is sourrounded by three dichloromethane lattice solvent molecules and two disordered perchlorate counter anions. At 180 K, the coordination environment of the iron(II) metal ion can be described as a distorted octahedron. The average Fe–N bond lengths varying from 1.889 Å to 1.980 Å indicate the LS state of the iron(II) ion at 180 K. The oxygen atoms of the thioacetyl units exhibit the following intermolecular hydrogen-bond interactions with pyrazole and pyridine hydrogen atoms:  $d(O1\cdotsH1A_{pyrazole}) = 2.392$  Å,  $d(O2\cdotsH7A_{pyridine}) =$ 2.407 Å,  $d(O2\cdotsH9A_{pyrazole}) = 2.446$  Å. The sulfur atoms of the thioacetyl units also show short contacts with the pyr-



Figure 1. ORTEP (50% probability) plot of molecular complex 1 with atomic labels. Hydrogen atoms, perchlorate counteranions and dichloromethane lattice solvent molecules are omitted for clarity. Selected bond lengths [Å]: Fe-N(1) 1.980(4), Fe-N(3) 1.892(4), Fe-N(5) 1.971(4), Fe-N(6) 1.969(4), Fe-N(8) 1.889(4), Fe-N(10) 1.959(4). Selected bond angles [°]: N(8)-Fe-N(3) 177.71(18), N(3)-Fe-N(6) 100.46(16), N(10)-Fe-N(6) 159.76(15), N(8)-Fe-N(5) 102.12(17), N(5)-Fe-N(1) 160.03(16), N(8)-Fe-N(10) 80.10(16), N(3)-Fe-N(10) 99.79(16), N(8)-Fe-N(6) 79.68(16), N(3)-Fe-N(5) 80.17(16), N(10)-Fe-N(5) 91.47(17), N(6)-Fe-N(5) 91.86(17), N(8)-Fe-N(1) 97.76(17), N(3)-Fe-N(1) 79.95(17), N(6)-Fe-N(1) 93.59(17).

azole hydrogen atom  $[d(S1 \cdots H9A_{pyrazole}) = 2.899 \text{ Å}]$  and pyridine carbon atom  $[d(S2 \cdots C28) = 3.368 \text{ Å}]$ . The two ace-tyl-protected thiol end groups are situated at a distance  $d(S1 \cdots S2)$  of 2.6 nm.

The temperature-dependent bulk magnetic measurement of molecular wire 1 in the range of 4.5-380 K is shown in Figure 2. The measurements were performed both at heating ( $\uparrow$ ) and cooling ( $\downarrow$ ) cycles, which revealed a reversible ST behaviour with a hysteresis loop. At 380 K the value of  $\chi T$  is 3.25 emu K mol<sup>-1</sup>, which is close to the expected value for an HS iron(II) ion in the S = 2 state. The ST temperatures for the heating  $(T_{1/2} \uparrow = 273 \text{ K})$  and cooling  $(T_{1/2} \downarrow \downarrow)$ = 281 K) modes revealed the occurrence of a ca. 8 K wide thermal hysteresis loop. Below ca. 200 K, the  $\gamma T$  value is almost constant and reached a minimum value of 0.07 emu K mol<sup>-1</sup> at 4.5 K, indicating the LS state of complex 1. This is also in good agreement with the low-spin state observed in the single-crystal data at 180 K. The spin transition is not lattice-solvent-assisted since the air-dried powder sample exhibits a very similar ST behaviour.



Figure 2.  $\chi T$  vs. T plot for complex 1 from 4.5 to 380 K ( $\downarrow$  cooling mode and  $\uparrow$  heating mode) measured with a 0.1 T applied DC magnetic field. The sample was cooled from 300 to 4.5 K, and the  $\chi T$  was first measured upon warming from 4.5 to 380 K, followed by the cooling mode.

#### Conclusions

We have designed, synthesized and characterized for the first time a novel iron(II) ST complex bearing acetyl-protected thiol anchor groups. The X-ray structure of complex 1 in the LS state revealed a distance of separation of 2.6 nm between the two thiol end groups. The molecular complex undergoes a thermally reversible ST at 277 K with a hysteresis loop width of ca. 8 K. Investigations of the tunable electronic transport through the molecular ST unit at the single-molecule level is in progress.<sup>[12]</sup>

#### **Experimental Section**

**Materials:** All reagents and solvents used in this study are commercially available and were used without further purification. 4-Iodo-1-(thioacetyl)benzene and 4-iodo-2,6-di(pyrazol-1-yl)pyridine were synthesized according to reported procedures.<sup>[11,2]</sup> <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data were recorded with a Bruker DPX 300

spectrometer with solvent-proton signal as internal standard. Infrared spectra were recorded using KBr-pressed pellets with a Perkin-Elmer Spectrum GX FT-IR spectrometer. MALDI-TOF MS data were acquired with a Voyager-DE PRO Bio spectrometry workstation. Elemental analyses were carried out with a Vario Micro cube. X-ray data collection was performed with a STOE IPDS II diffractometer with graphite-monochromated Mo- $K_a$  radiation at 180 K. The structure was solved by direct methods (SHELX-97). Refinement was done with anisotropic temperature factors for all non-hydrogen atoms. Temperature-dependent static susceptibilities of 1 were recorded with an MPMS-5S (Quantum Design) SQUID magnetometer over a temperature range of 4.5-380 K in a homogeneous 0.1 T external magnetic field. Gelatin capsules were used as sample containers. The diamagnetic corrections of the molar magnetic susceptibilities were applied using well-known Pascal's constants. Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive; only small quantities of such compounds should be prepared and handled with much care!

**Crystal Data for 1:**  $C_{45}H_{36}Cl_8FeN_{10}O_{10}S_2$ ; triclinic; space group  $P\bar{1}$ ; a = 10.831(2) Å; b = 13.480(3) Å; c = 19.774(4) Å;  $a = 76.50(3)^\circ$ ;  $\beta = 82.62(3)^\circ$ ;  $\gamma = 70.39(3)^\circ$ ; V = 2640.3(9) Å<sup>3</sup>; crystal size  $= 0.22 \times 0.11 \times 0.06$  mm; index ranges:  $-12 \le h \le 12$ ,  $-15 \le k \le 15$ ,  $-23 \le l \le 22$ ;  $\theta$  range for data collection:  $1.64-24.72^\circ$ ; completeness to  $\theta$ : 97.1%; Z = 2;  $D_{obsd.} = 1.611$  g/m<sup>3</sup>; F(000) = 1300; reflections with  $I > \sigma(I) = 5876$ ;  $\mu = 0.836$  mm<sup>-1</sup>;  $R(F_o) = 0.0644$ ;  $R_w(F) = 0.1623$ ; GOF on  $F^2 = 1.026$ ; T = 180(2) K. CCDC-668334 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif.

2,6-Di(pyrazol-1-yl)-4-(trimethylsilylethynyl)pyridine (3): Freshly distilled dry diisopropylamine (150 mL) was placed into a 250 mL Schlenk vessel, and nitrogen was bubbled through it for 30 min. 4-Iodo-2,6-di(pyrazol-1-yl)pyridine (4 g,11.9 mmol),  $Pd(PPh_3)_4$ (1.38 g, 1.2 mmol) and CuI (228 mg, 1.2 mmol) were added, and nitrogen was bubbled through the mixture for another 1 h. (Trimethylsilyl)acetylene (7 mL, 52 mmol) was added dropwise to this mixture with a syringe through a septum while stirring was continued at room temperature under nitrogen for 3 d. An additional portion of (trimethylsilyl)acetylene (4 mL, 30 mmol) was added dropwise, and the mixture was stirred at room temperature for another 3 d. The workup procedure has to be taken carefully to avoid both the presence of strong bases and temperatures above 40 °C. The solvent was removed in vacuo by rotary evaporation, and the obtained black crude solid was purified by column chromatography on neutral alumina using a mixture of ethyl acetate/hexane (1:50) as eluent. The colourless, blue-fluorescent fraction ( $R_{\rm f} = 0.43$ ) was concentrated to afford 3.4 g (11.1 mmol, 93% yield) of white crystalline **3**. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 0.29$  [s, 9 H,  $(CH_3)_3Si$ ], 6.51 (td,  ${}^{3}J$  = 2.4,  ${}^{4}J$  = 0.9 Hz, 2 H, pyrazole), 7.78 (d,  ${}^{3}J = 1.5$  Hz, 2 H, pyrazole), 7.91 (s, 2 H, pyridine), 8.55 (dd,  ${}^{3}J =$ 2.4,  ${}^{4}J = 0.6$  Hz, 2 H, pyrazole) ppm.  ${}^{13}C$  NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = -0.26$  [(CH<sub>3</sub>)<sub>3</sub>Si], 101.4 (C=C), 101.6 (C=C), 108.3, 111.9, 127.2, 136.6, 142.7, 150.3 ppm. FT-IR (KBr):  $\tilde{v} = 3156$ , 3115, 2955, 2898, 2171, 1722, 1615, 1554, 1464, 1398, 1252, 1206, 1109, 1044, 894, 847, 754 cm<sup>-1</sup>. MALDI-TOF: experiment: m/z (relative intensity of isotopic distribution) = 496.63 (100%), 497.63(35%), 498.63 (15%); simulation: m/z (relative intensity of isotopic distribution) = 496.19 (100%), 497.19 (35%), 498.19 (5%).

**4-Ethynyl-2,6-di(pyrazol-1-yl)pyridine (4):** Compound **3** (2 g, 6.5 mmol) was dissolved in dichloromethane (80 mL) followed by the addition of methanol (80 mL). Potassium carbonate (7 g,

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50 mmol) was added to this mixture, and it was stirred at room temperature overnight (18 h). The solvents were evaporated from the yellowish solution in vacuo by rotary evaporation, and the crude solid was purified by column chromatography on neutral alumina using ethyl acetate/hexane (1:40) as eluent to afford 1.3 g (85% yield) of **4** as white crystalline solid. <sup>1</sup>H NMR (300 MHz,CDCl<sub>3</sub>, 25 °C):  $\delta$  = 3.38 (s, 1 H, C=H), 6.50 (td, <sup>3</sup>J = 2.7,  ${}^{4}J = 0.6$  Hz, 2 H, pyrazole), 7.76 (dd,  ${}^{3}J = 1.5$ ,  ${}^{4}J = 0.6$  Hz, 2 H, pyrazole), 7.92 (s, 2 H, pyridine), 8.53 (dd,  ${}^{3}J = 2.7$ ,  ${}^{4}J = 0.6$  Hz, 2 H, pyrazole) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 80.84 (C=C), 83.11 (C=C), 108.58, 112.33, 127.43, 135.86, 142.99, 150.55 ppm. FT-IR (KBr):  $\tilde{v} = 3217, 3157, 3106, 2727, 2109, 1758,$ 1612, 1557, 1526, 1473, 1401, 1266, 1209, 1108, 1047, 955, 867, 749 cm<sup>-1</sup>. MALDI-TOF: experiment: m/z (relative intensity of isotopic distribution) = 496.63 (100%), 497.63 (35%), 498.63 (15%);simulation: m/z (relative intensity of isotopic distribution) = 496.19 (100%), 497.19 (35%), 498.19 (5%).

S-(4-{[2,6-(Dipyrazol-1-yl)pyrid-4-yl]ethynyl}phenyl) Ethanethioate (L): 4 (1.08 g, 4.6 mmol), 4-iodo-1-(thioacetyl)benzene (1.02 g, 3.7 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (145 mg, 180 µmol) and CuI (70 mg, 370 µmol) were placed into a 100 mL Schlenk tube, and the mixture was purged with nitrogen several times. To this mixture were added 20 mL each of freshly distilled thf and diisopropylamine, and the reaction mixture was stirred at room temperature for 3 d. Acetic anhydride (8 mL) was added to the reaction mixture, and all solvents were removed in vacuo by rotary evaporation. The dark and resinous crude reaction product was purified by column chromatography on silica gel using a mixture of ethyl acetate/hexane (1:4) as eluent to afford a mustard-coloured solid, which needed a second chromatographic purification on silica with a mixture of ethyl acetate/hexane (1:9) as eluent. The yellow-brownish product with  $R_{\rm f} \approx 0.37$  (ethyl acetate/hexane, 1:4) was recrystallized from hot diethyl ether to afford 0.28 g (20% yield with respect to the iodo compound) of a yellowish crystalline material which was suitable for single-crystal X-ray diffraction. <sup>1</sup>H NMR (300 MHz,  $CDCl_3$ , 25 °C):  $\delta = 2.44$  (s, 3 H,  $CH_3COS$ ), 6.50 (m, 2 H, pyrazole), 7.50 (dd,  ${}^{3}J = 43.5$ ,  ${}^{4}J = 8.1$  Hz, 4 H, phenyl), 7.77 (d,  ${}^{3}J = 1.5$  Hz, 2 H, pyrazole), 7.96 (s, 2 H, pyridine), 8.55 (d,  ${}^{3}J$  = 2.4 Hz, 2 H, pyrazole) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 30.76 (CH<sub>3</sub>), 88.32 (C≡C), 94.42 (C≡C), 108.6, 111.8, 123.4, 127.5, 130.0, 133.0, 134.7, 136.7, 143.0, 150.6, 193.50 (C=O) ppm. FT-IR (KBr):  $\tilde{v} = 3109$ , 2924, 2854, 2220, 1696, 1608, 1553, 1468, 1398, 1261, 1208, 1123, 1042, 955, 863, 762 cm<sup>-1</sup>. MALDI-TOF: experiment: m/z (relative intensity of isotopic distribution) = 496.63 (100%), 497.63 (35%), 498.63 (15%); simulation: m/z (relative intensity of isotopic distribution) = 496.19 (100%), 497.19 (35%),498.19 (5%).

**Bis[S-(4-{[2,6-(dipyrazol-1-y])pyrid-4-yl]ethynyl}phenyl)ethanethioato]iron(II) Diperchlorate (1):** In a 100 mL round-bottomed flask ligand L (67 mg, 0.17 mmol) was dissolved in dichloromethane (15 mL), and methanolic Fe(ClO<sub>4</sub>)<sub>2</sub> hydrate (32 mg, 0.085 mmol) was added to the ligand solution. The mixture was stirred at room temperature for 15 min, and then a portion of dichloromethane (10 mL) was added, after which formation of a slight precipitate was observed. The precipitate was filtered off and discarded. Methanol (5 mL) and dichloromethane (15 mL) were added to the filtrate, and the mixture was left at room temperature overnight to obtain dark red crystals (56 mg, yield 58%). FT-IR (KBr):  $\tilde{v} =$ 3122, 2220, 1696, 1620, 1558, 1527, 1457, 1406, 1268, 1217, 1093, 971, 833, 767, 624 cm<sup>-1</sup>. C<sub>42</sub>H<sub>30</sub>Cl<sub>2</sub>FeN<sub>10</sub>O<sub>10</sub>S<sub>2</sub>·1/3CH<sub>2</sub>Cl<sub>2</sub>· 1/3CH<sub>3</sub>OH (1064.62): calcd. C 48.13, H 3.03, N 13.16, S 6.02; found C 48.12, H 3.09, N 13.13, S 6.22.

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